

PROCESS FOR COMBUSTION OF A LIQUID HYDROCARBON

The invention is directed to a process for combustion of a liquid hydrocarbon fuel wherein the following steps are performed:

- (a) obtaining a mixture of liquid hydrocarbon droplets in an oxygen containing gaseous phase,
- 5 (b) evaporating the liquid hydrocarbon droplets, preferably in a cool flame at a temperature of between 300 and 480 °C, to obtaining a gaseous mixture comprising oxygen and hydrocarbons, and
- 10 (c) total combustion of the gaseous mixture obtained in step (b).

Such a process is described in detail in High Modulation Burner for Liquid Fuels Based on Porous Media Combustion and Cool Flame Vaporization; D. Trimis, 15 K. Wawrzinek, O. Harzfeld, K. Lucka, A. Rutsche, F. Haase, K. Krüger, C. Küchen, Sixth International Conference on Technologies and Combustion for a Clean Environment (Clean Air VI), Vol. 2, Paper 23.1, Porto, Portugal, 9-12 July 2001. This article describes a so-called porous burner, which comprises means to mix air and a liquid fuel, a space for evaporating the liquid fuel in a cool flame, and a space filled with a porous material in which the combustion of the air/evaporated fuel mixture takes place. As a possible liquid fuel 20 Industrial Gas Oil is mentioned in this article. Means to de-sulphurise the exhaust gas are also present, e.g. in a water-bath. Typical for these types of burners is that they are very suited for low power applications in the range of 2 to 30 kW. This makes them very suited for 25

domestic applications such as domestic heating or boiler applications. A further advantage is these types of burners allow a high power modulation of more than 1:10. This allows a reduction of start/stop events with its associated temporally higher emissions of hydrocarbons and carbon monoxide.

A disadvantage of the use of Industrial Gas Oil is that the fuel does not easily evaporate in the evaporator space of the burner. Non-complete evaporation of the liquid fuel will result in more emissions in the flue gas leaving the burner. Additionally non-complete evaporation may result in deposits in the combustion zone and downstream heat exchanger surfaces. This may result in a decrease of efficiency in the heat exchanger, in incomplete combustion or uncontrolled flame ignition.

The objective of the present invention is therefore to provide a process, which does not have such a disadvantage. This object is achieved with the following process.

Process for combustion of a liquid Fischer-Tropsch derived hydrocarbon fuel wherein the following steps are performed:

- (a) obtaining a mixture of liquid hydrocarbon droplets in an oxygen containing gaseous phase,
- (b) evaporating the liquid hydrocarbon droplets to obtaining a gaseous mixture comprising oxygen and hydrocarbons, and
- (c) total combustion of the gaseous mixture obtained in step (b).

Applicants found that by using a Fischer-Tropsch derived fuel a better evaporation takes place in the cool flame. This has resulted in a better combustion, improved flame ignition and less fouling of any downstream heat

exchanger surfaces. Furthermore because Fischer-Tropsch derived fuels contain almost no sulphur no special measures have to be provided to clean the flue gas of said combustion or to apply special non-corrosive

5 materials.

In step (a) a mixture of liquid Fischer-Tropsch derived fuel droplets in a gaseous continuous phase is prepared. The gaseous phase will contain oxygen or any other oxidant. The gaseous phase is preferably air. The 10 preparation of said mixture may be performed by different techniques. For example a mixture is obtained by passing a mixture of air and liquid fuel through small openings at a certain pressure difference resulting in the formation of the small liquid droplets in the gaseous 15 phase. A second technique is by atomization of the liquid fuel through ultrasonic vibrations as for example described in US-A-US4264837. A preferred method is wherein the liquid fuel is first atomised by means of a spray nozzle and subsequently mixed with air as for 20 example described in the above-cited article.

The size of the droplets will be determined by the method chosen. In case of a nozzle the dimensions of the nozzle, the fuel feed rate, fuel oil pressure, fuel viscosity (and therefore temperature of the fuel) and 25 surface tension will influence the droplet size. Smaller droplets and thus a better evaporation of the liquid fuel will be achieved at higher fuel feed rates and/or higher oil pressures for a given feed nozzle. Preferably the droplet size is as small as possible. However the high 30 pressures needed to obtain such small droplets may be not economically or technically feasible. Applicants have found that when using Fischer-Tropsch derived fuel larger droplets may be allowed without negatively affecting the

combustion. This is very advantageous because now a lower oil pressure may be applied which makes the combustion process technically more simple and more energy efficient.

5 The oxygen containing gas will normally be air. However other sources of oxygen containing gases such as purified oxygen could also be used. For the remainder of this description reference shall be made to air, thereby not excluding the alternative sources. The excess air 10 ratio in the present process is preferably between 1.1 and 3 (excess air ratio is defined as the ratio between the actual air supply and the needed air for stoichiometric combustion of the fuel ( $\lambda=1$ )). The liquid fuel is preferably introduced into the air as a fine spray of 15 droplets.

Step (b) is preferably performed by means of a so-called cool flame. Cool flames, sometimes also referred to as cold flames, start at a temperature of 300 °C and stabilize, virtually independent of the air ratio, at a 20 temperature of 480 °C at 1 bar conditions. A cool flame will be formed when at a certain minimum temperature (300 °C). If the temperature is kept below 480 °C no auto ignition will occur because the needed activation energy is too high under these conditions. This temperature is 25 suitably maintained by means of indirect heat exchange against either hot exhaust gasses or against the combustion zone. In the cool flame the liquid droplets will evaporate thereby forming a gaseous mixture that is used in step (c). Steps (b) and (c) in the method according to the present invention are physically 30 separated. Preferably measures are taken to avoid hot combustion gases from step (c) to enter the area wherein the cool flame is present. Examples of such measures are

flame traps through for example flow acceleration or metal grids positioned at the physical interface between step (a) and step (b). Examples of cool flames are described in the above referred to article and in

5 EP-A-947769.

Alternatively steps (a) and (b) may be performed by first evaporation of the fuel and subsequently mixing the gaseous fuel with the oxygen containing mixture, or by evaporation in an inert medium before mixing with the

10 oxygen containing gas.

The combustion in step (c) may be performed in different manners. For example aerodynamic stabilization of the flame may be applied. More preferably the flame is positioned by means of a porous surface, wherein the mixture is provided to one end of said surface and a flame is present just down stream of said surface. An example of such a surface burner is described in

15 EP-A-947769.

Another preferred embodiment for step (c) is wherein the combustion takes place in a porous material as for example described in the above referred to article. The porous material may be as described in the above-described article or as in US-A-5522723. It has been found important that combustion process may take place inside the porous structure. Too small pores will quench the flame and too large pores will cause flame propagation. Preferably the porous material is comprised of a first zone wherein flame propagation is suppressed, the so-called pre-heating zone and a second zone wherein flame propagation is possible, the actual combustion zone. The porous material may be made from for example alumina, zirconium oxide or silicium carbide.

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In step (c) preferably a flame detector is used. Examples of suitable detectors are the UV sensors and IR sensors. A more preferred detector is the so-called ionisation sensor. An ionisation sensor is suitable to monitor burners with intermittent operation as well as continuous operation. The principle of operation of the ionisation flame monitor is based on the rectifying effect of a flame. If a flame is present, a current flows between the burner and the ionisation electrode. This ionisation current is evaluated by the flame monitor to determine if a flame is present. In some prior art applications ionisation sensors could not be used in combination with a liquid fuel because deposits in the sensor led to false currents in the sensor. Because use of the Fischer-Tropsch derived fuel, especially a fuel composition not containing a metal based combustion improver results in less deposits ionisation sensors can be applied. Examples of metal based combustion improvers are ferrocene based additives and methylcyclopentadienylmanganese-tricarbonyl (MMT). This is an advantage because these sensors are more readily available than the IR or UV sensors.

The Fischer-Tropsch derived fuel will comprise a Fischer-Tropsch product which may be any fraction of the middle distillate fuel range, which can be isolated from the (hydrocracked) Fischer-Tropsch synthesis product. Typical fractions will boil in the naphtha, kerosene or gas oil range. Preferably a Fischer-Tropsch product boiling in the kerosene or gas oil range is used because these products are easier to handle in for example domestic environments. Such products will suitably comprise a fraction larger than 90 wt% which boils between 160 and 400 °C, preferably to about 370 °C.

Examples of Fischer-Tropsch derived kerosene and gas oils are described in EP-A-583836, WO-A-9714768, WO-A-9714769, WO-A-011116, WO-A-011117, WO-A-0183406, WO-A-0183648, WO-A-0183647, WO-A-0183641, WO-A-0020535, WO-A-0020534, EP-A-1101813, US-A-5766274, US-A-5378348, US-A-5888376 and US-A-6204426.

The Fischer-Tropsch product will suitably contain more than 80 wt% and more suitably more than 95 wt% iso and normal paraffins and less than 1 wt% aromatics, the balance being naphthenics compounds. The content of sulphur and nitrogen will be very low and normally below the detection limits for such compounds. This low content of these elements is due to the specific process wherein the Fischer-Tropsch reaction is performed. The content of sulphur will therefore be below 5 ppm and the content of nitrogen will be below 1 ppm. As a result of the low contents of aromatics and naphthenics compounds the density of the Fischer-Tropsch product will be lower than the conventional mineral derived fuels. The density will be between 0.65 and 0.8 g/cm<sup>3</sup>.

The fuel used in the process of the present invention may also comprise fuel fractions other than the Fischer-Tropsch product. Examples of such fractions may be the kerosene or gas oil fractions as obtained in traditional refinery processes, which upgrade crude petroleum feedstock to useful products. Preferred non-Fischer-Tropsch fuel components are the ultra low sulphur (e.g. less than 50 ppm sulphur) kerosene or diesel fractions, which are currently on the market. Optionally non-mineral oil based fuels, such as bio-fuels, may also be present in the fuel composition. The content of the Fischer-Tropsch product in the fuel will be preferably be above 40 wt%, more preferably above 60 wt% and most preferably

above 80 wt%. It should be understood that the content of such, currently less available, Fischer-Tropsch product will be optimised, wherein pricing of the total fuel will be balanced with the advantages of the present invention. For some applications fuels fully based on a Fischer-Tropsch product plus optionally some additives may be advantageously used.

The fuel may also comprise one or more of the following additives. Detergents, for example OMA 350 as obtained from Octel OY; stabilizers, for example Keropon ES 3500 as obtained from BASF Aktiengesellschaft, FOA 528A as obtained from OCTEL OY; metal-deactivators, for example IRGAMET 30 (as obtained from Specialty Chemicals Inc; (ashless) dispersants, for example as included in the FOA 528 A package as obtained from Octel OY; anti-oxidants: IRGANOX L06, or IRGANOX L57 as obtained from Specialty Chemicals Inc; cold flow improvers, for example Keroflux 3283 as obtained from BASF Aktiengesellschaft, R433 or R474 as obtained from Infineum UK Ltd; anti-corrosion: Additin RC 4801 as obtained from Rhein Chemie GmbH, Kerocorr 3232 as obtained from BASF, SARKOSYL 0 as obtained from Ciba; reodorants, for example Compensol as obtained from Haarmann & Reimer; biocides, for example GROTA MAR 71 as obtained from Schuelke & Mayr; lubricity enhancers, for example OLI 9000 as obtained from Octel; dehazers, for example T-9318 from Petrolite; antistatic agents, for example Stadis 450 from Octel; and foam reducers, for example TEGO 2079 from Goldschmidt. It has been found that the Fischer-Tropsch derived fuel does not necessarily have to contain a combustion improver such as for example ferrocene or MMT.

The Fischer-Tropsch product is colourless and odourless. For safety reasons an odour marker, as for example applied in natural gas for domestic consumption, may be present in the Fischer-Tropsch derived fuel. Also 5 a colour marker may be present to distinguish the fuel from other non-Fischer-Tropsch derived fuels.

The total content of the additives may be suitably between 0 and 1 wt% and preferably below 0.5 wt%.

The combustion process using the Fischer-Tropsch fuels is preferably applied for domestic heating, wherein 10 the heat of combustion is used to heat water by indirect heat exchange in so-called boilers. The process is especially suited for domestic applications because of its power modulation range of between 2 and 30 kW. The 15 heated water may be used to warm up the house or consumed in for example showers and the like.

The combustion process using the Fischer-Tropsch fuels may advantageously be further used for direct 20 heating of large spaces. Such applications are characterized in that the flue gasses are directly supplied to said space to heat up said space. Spaces such a tents and halls are often heated up with such an apparatus. Normally gaseous fuels for example natural 25 gas, LPG and the like, are used for this application because the associated flue gasses can be safely supplied to said space. A disadvantage of the use of gaseous fuels is however that handling of the pressurized gas containers and combustion equipment requires professional 30 skills in order to operate such an apparatus safely. By using a Fischer-Tropsch derived liquid fuel a comparable flue gas is obtained in the combustion process as when a gaseous fuel is used. Thus a method is provided wherein a liquid fuel can be applied for direct heating of spaces.

The application of the liquid Fischer-Tropsch derived fuel makes the use of the apparatus for direct heating much more simple and safe.

5 The direct heating of spaces is preferably performed by means of a so-called radiation heater. In such an apparatus step (c) is preferably performed at or in the surface of a perforated plate. This plate is preferably a ceramic plate. In this plate combustion will take place in the short channels across the plate. The combustion heat will result in a glowing plate generating radiation energy that will heat up the surrounding air. Typically 10 the fuel for such radiation heaters is a gaseous fuel because the flue gasses will also be emitted in the surrounding air. Applicants have now found that also a 15 Fischer-Tropsch fuel may be advantageously applied without the disadvantages of a liquid fuel. Examples of radiation heaters which normally operate on a gaseous fuel but which now can be operated on a liquid fuel are described in US-A-5139415, EP-A-0949452 or EP-A-0037046.

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porous surface. The radiant heat developed at the surface of such heaters will heat the environment in which it is placed.

The process may also be advantageously applied in a process to generate steam. Especially when step (c) is performed in a porous material as described in for example US-A-5522723. The heat of combustion generated by such process can be used to generate steam, which may be used for various purposes, such as heating. A preferred application is described in US-A-2002194848 and WO-A-03036072, wherein said generated steam is first super heated and subsequently fed to a piston engine or an expansion engine. This application is sometimes also referred to as the SteamCell of Enginion AG (SteamCell is a trademark). The engine may provide mechanical power, for example to power an automobile, or electricity. The claimed advantage of this type of engine is low NO<sub>x</sub> emissions as compared to the state of the art combustion engines. By using a Fischer-Tropsch derived fuel NO<sub>x</sub> emissions may be further reduced in such an application. An additional advantage is that the Fischer-Tropsch derived fuel is practically sulphur free. This can further simplify the design of the burner and reduce the complexity of such an engine.